Vital Theorem - Classical Systems Only

Consider \( \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int d\mathbf{q} d\mathbf{p} \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\int d\mathbf{q} d\mathbf{p} \; e^{-\beta H}} \)

where \( x_i, p_j \) are any of the GN generalized coordinates \( q, p \) \( i = 1, \ldots, 3N \).

\[
\frac{\int d\mathbf{q} d\mathbf{p} \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\int d\mathbf{q} d\mathbf{p} \; e^{-\beta H}} = \frac{\int d\mathbf{q} d\mathbf{p} \; x_i \frac{\partial H}{\partial x_j} (e^{-\beta H})}{\int d\mathbf{q} d\mathbf{p} \; (e^{-\beta H})}
\]

Integrate by parts with respect to \( x_j \) to be assumed from now on, \( \frac{1}{\beta} \int d\mathbf{q} d\mathbf{p} \; x_i e^{-\beta H} \int_{x_j^{(1)}}^{x_j^{(2)}} x_j^{(2)} - x_j^{(1)} \frac{\partial}{\partial x_j} (e^{-\beta H}) \)

\( \frac{1}{\beta} \int d\mathbf{q} d\mathbf{p} \; (\frac{\partial}{\partial x_j}) (e^{-\beta H}) \)

\( \int_{x_j^{(1)}}^{x_j^{(2)}} \)

Integral over all coordinates except \( x_j \)

The boundary integral vanishes because \( H \) becomes infinite at the extremal values of any coordinate.

- If \( x_j \) is a momentum \( p_j \), then extremal values are \( p_j = \pm \infty \) and \( H \propto p_j^2 / m \rightarrow \infty \).

- If \( x_j \) is a spatial coordinate \( q_j \), then extremal values are at boundary of system, while the potential energy confining the particle to the volume \( V \) becomes infinite.

\[
\Rightarrow \int d\mathbf{q} d\mathbf{p} \; x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int d\mathbf{q} d\mathbf{p} \; (\frac{\partial x_i}{\partial x_j}) e^{-\beta H}
\]
but \( \frac{\partial x_i}{\partial x_j} = \delta_{ij} \)

\[ \Rightarrow \quad \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta} \delta_{ij} \sum_{k} \sum_{k'} e^{-\beta H_{kk'}} \sum_{k''} \sum_{k'''} e^{-\beta H_{kk''}} \]

\[ \langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij} \quad \Leftrightarrow \quad \text{Virial Theorem} \]

If \( x_i = x_j = p_i \), then

\[ \langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \delta_i \rangle = k_B T \]

If \( x_i = x_j = q_i \), then

\[ \langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i p_i \rangle = k_B T \]

Where we used Hamilton's equations of motion

\[ \frac{\partial H}{\partial p_i} = \dot{q}_i \quad \text{and} \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i \]

\[ \Rightarrow \quad \langle \sum_{i=1}^{3N} p_i \dot{q}_i \rangle = 3 N k_B T \]

\[ -\langle \sum_{i=1}^{3N} q_i \dot{p}_i \rangle = 3 N k_B T \quad \text{Virial Theorem} \]

Clausius (1870)
Ergun's theorem - Classical systems only

Suppose the Hamiltonian is quadratic in:
Some particular degree of freedom $x_j$ ($x_j$ is either a coord or a momentum)

$$H[S_i, P_i] = H'[S_i, P_i] + \alpha_j x_j^2$$

Depends on all degrees of freedom except $x_j$

Then $\langle H \rangle = \langle H' \rangle + \alpha j \langle x_j^2 \rangle$

Contribution to total average energy from the degree of freedom $x_j$

$$\langle x_j^2 \rangle = \frac{\prod_i \int dq_i dp_i x_j^2 e^{-\beta(H' + \alpha_j x_j^2)}}{\prod_i \int dq_i dp_i e^{-\beta(H' + \alpha_j x_j^2)}}$$

$$= \frac{(\prod_i \int dq_i dp_i e^{-\beta H'}) \int dx_j x_j^2 e^{-\beta \alpha_j x_j^2}}{(\prod_i \int dq_i dp_i e^{-\beta H'}) \int dx_j e^{-\beta \alpha_j x_j^2}}$$

where $\prod_i$ is over all degrees of freedom except $x_j$
\[ \langle x_j^2 \rangle = \frac{\int dx_j \, x_j^2 e^{-\beta \alpha_j x_j^2}}{\int dx_j \, e^{-\beta \alpha_j x_j^2}} = \frac{1}{2 \beta \alpha_j} = \frac{1}{2} \frac{k_B T}{\alpha_j} \]

(follows from \( \int dx \, e^{-x^2/\sigma^2} = \sqrt{2\pi \sigma^2} \) and \( \int dx \, \frac{x^2 e^{-x^2/2\sigma^2}}{\sqrt{2\pi \sigma^2}} = \sigma^2 \))

So the contribution to \( \langle H \rangle \) from the degree of freedom \( x_j \)

\[ \alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T \]

\Rightarrow each quadratic degree of freedom in the Hamiltonian contributes \( \frac{1}{2} k_B T \) to the total average energy.

Ideal gas: \( H = \sum_{i=1}^{N} \frac{1}{2m} p_i^2 \)

There are \( 3N \) quadratic degrees of freedom:
the three momenta \( p_i \) components for each particle

\[ \Rightarrow E = \langle H \rangle = \frac{3N}{2} k_B T \]

or average energy per particle

\[ \langle E \rangle = \frac{E}{N} = \frac{3}{2} k_B T \]

as we saw earlier from the simple kinetic theory of the ideal gas.
Elastic Vibrations of a Solid

We can imagine the Hamiltonian for the periodic array of atoms in a solid to be

\[ H = \sum_i \frac{\hat{p}_i^2}{2M} + \frac{1}{2} \sum_{ij} U(\vec{r}_i - \vec{r}_j) \]

pair-wise interactions between the atoms.

The position of atom \( i \) can be written as

\[ \vec{r}_i = \vec{R}_i + \vec{u}_i \]

where \( \vec{R}_i \) is its position in the perfect periodic array, and \( \vec{u}_i \) is a small displacement from this position due to thermal fluctuations.

Then we can expand

\[ U(\vec{r}_i - \vec{r}_j) = U(\vec{R}_i - \vec{R}_j + \vec{u}_i - \vec{u}_j) \]

\[ = U(\vec{R}_i - \vec{R}_j) + \nabla U \cdot (\vec{u}_i - \vec{u}_j) + \frac{1}{2} \nabla^2 U \cdot (\vec{u}_i - \vec{u}_j)^2 \]

\[ + \frac{1}{2} \sum_{\alpha,\beta=1}^3 \nabla_{\alpha} U \cdot \nabla_{\beta} U \cdot (\vec{u}_i - \vec{u}_j)(\vec{u}_i - \vec{u}_j) \]

Now assume the positions \( \vec{R}_i \) describe a stable equilibrium in the mechanical sense (i.e., the net force on each atom is zero), then

\[ \sum_{j \neq i} \nabla U \cdot (\vec{u}_i - \vec{u}_j) = 0 \]
The Hamiltonian is then

\[
\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{ij} \sum_{\alpha \beta} \frac{1}{2} \frac{\partial^2 u(r_i, r_j)}{\partial x_i^{\alpha} \partial x_j^{\beta}} (u_{i\alpha} - y_{i\alpha}) (u_{j\beta} - y_{j\beta}) + \text{constant}
\]

We see that \( \mathcal{H} \) is quadratic in the displacements \( u_i \).

We can rewrite the above as

\[
\mathcal{H} = \sum_i \frac{p_i^2}{2m} + \sum_{ij} \sum_{\alpha \beta} D_{ij}^{\alpha \beta} u_i^{\alpha} y_{j\beta}
\]

where the "dynamical matrix" \( D \) is related to the \( \frac{\partial^2 u}{\partial x_i^{\alpha} \partial x_j^{\beta}} \).

One can show that it is always possible to choose "normal coordinates" \( \tilde{u}_i^{\alpha} = \sum_{\beta} C_{ij}^{\alpha \beta} u_j^{\beta} \) such that the above quadratic form is diagonalized.

(See Ashcroft & Mermin for details.)

Equation Theorem then says that each momentum \( \pi_i^{\alpha} \) gives \( \frac{1}{2} k_B T \) and each normal coord \( \tilde{u}_i^{\alpha} \) also gives \( \frac{1}{2} k_B T \).

\Rightarrow \text{each of the } 6N \text{ degrees of freedom gives } \frac{1}{2} k_B T \text{ towards the total average internal energy.}

\Rightarrow E = \langle \mathcal{H} \rangle = \langle 6N \rangle \frac{1}{2} k_B T = \boxed{3Nk_B T} = E
The contribution to the specific heat of a solid, due to atomic vibrations, is therefore

\[ C_V = \frac{\partial E}{\partial T} = 3Nk_B \]  

Law of Dulong + Petit

The classical result predicts a $C_V$ that is independent of temperature. In real life, however, one finds

\[ C_V \]

at low $T$, see a clear decrease from Dulong-Petit prediction. Unexplainable classically

It was one of the early successes of quantum mechanics to explain why the Law of Dulong Petit fails at low $T$. This is an interesting example where the effects of quantum mechanics can be observed not in atomic phenomena but in the thermodynamics of macroscopic solids!

We will see the solution to this problem later, when we discuss the statistics of bosons.
Paramagnetism - Classical Spins

N distinguishable spins, we ignore interaction between spins and consider only the interaction of each spin with an external magnetic field \( \vec{H} \).

This could be a model for fixed magnetic impurities in a solid. The "spin" is the intrinsic magnetic dipole moment of the magnetic atom, that is fixed to sit at a particular spatial position (that the atoms cannot move is why we consider them distinguishable).

Hamiltonian of the \( N \)-spins is

\[
H = - \sum_{i=1}^{N} \vec{\mu}_i \cdot \vec{H} + \text{(spins are non-interacting)}
\]

Spin of atom \( i \)

energy is lowest when it is \( \| \) to \( \vec{H} \)

\[
= -\mu_0 h \sum_{i=1}^{N} \cos \Theta_i
\]

where \( \mu_0 = |\vec{\mu}_i| \) is fixed and \( \Theta_i \) is angle of \( \vec{\mu}_i \) with respect to \( \vec{H} \)
Spins are distinguishable

\[ \Rightarrow \quad Q_N = (Q_1)^N \quad \text{no factor} \quad \frac{1}{N!} \]

\[ Q_1 = \int_0^{2\pi} \int_0^\pi d\theta \sin \theta \quad e^{\beta \mu \vec{A} \cdot \vec{B}} \]

Integrate overall possible states of the single spin \( \vec{\mu} \), i.e., over all possible orientations of the vector \( \vec{\mu} \),

\[ Q_1 = 2\pi \int_0^\pi d\theta \sin \theta \quad e^{\beta \mu \vec{A} \cdot \vec{B}} \]

Make substitution of variable,

\[ x = -\cos \theta \]

\[ dx = \sin \theta \quad d\theta \]

\[ \theta = 0 \quad \Rightarrow \quad x = -1 \]

\[ \theta = \pi \quad \Rightarrow \quad x = +1 \]

\[ Q_1 = 2\pi \int_{-1}^{1} dx \quad e^{\beta \mu \vec{A} \cdot \vec{B}x} = \frac{2\pi}{\beta \mu} \left[ \frac{e^{\beta \mu \vec{A} \cdot \vec{B}} - e^{-\beta \mu \vec{A} \cdot \vec{B}}}{\beta \mu} \right] \]

\[ = \frac{4\pi}{\beta \mu} \sinh (\beta \mu \vec{A} \cdot \vec{B}) \]

\[ \sinh x = \frac{e^x - e^{-x}}{2} \]
Average total magnetization $\vec{M}$ is oriented $\parallel$ to $\vec{h}$. If we choose $\vec{h} = \hat{z}$ along $z$, then

$$M_z = N \langle \mu \cos \theta \rangle = \frac{N}{\beta} \frac{\partial}{\partial h} \left[ \frac{1}{2\pi} \int_0^{2\pi} \int_0^\pi \rho \sin \theta e^{\beta \mu \cos \theta} \sin \theta d\theta d\rho \right]$$

$$= \frac{N}{\beta} \frac{\partial}{\partial h} \left( \frac{1}{2\pi} \int_0^{2\pi} \int_0^\pi \rho \sin \theta e^{\beta \mu \cos \theta} \sin \theta d\theta d\rho \right)$$

$$= \frac{N}{\beta} \frac{\partial}{\partial h} \left( \frac{1}{2\pi} \int_0^{2\pi} \int_0^\pi \rho \sin \theta e^{\beta \mu \cos \theta} \sin \theta d\theta d\rho \right)$$

$$= \frac{\partial}{\partial h} \left[ k_B T \ln Q \right] = -\frac{\partial}{\partial h} A(T, h)$$

when we apply $\vec{h}$, the magnetic field $\vec{h}$ is a new thermodynamic variable. The above

$$M_z = -\frac{\partial A(T, h)}{2\pi}$$

says that total magnetization is the thermodynamic conjugate variable to magnetic field.
Using our result for $Q$, we get

$$
\frac{M_3}{N} = \frac{1}{\beta \partial h} (\ln Q) = \frac{1}{\beta} \frac{\partial Q}{\partial h}
$$

$$
= \frac{4\pi}{\beta} \left[ \frac{\coth (\beta \mu h) - \sinh (\beta \mu h)}{\beta \mu h} \right]
$$

$$
= \frac{4\pi \sinh (\beta \mu h)}{\beta \mu h}
$$

$$
= \mu h \left[ \frac{\coth (\beta \mu h)}{h} - \frac{1}{\beta \mu h^2} \right]
$$

$$
\frac{M_3}{N} = \mu \left[ \coth (\beta \mu h) - \frac{1}{\beta \mu h} \right]
$$

hyperbolic cotan

$$
\frac{M_3}{N} = \langle \mu_3 \rangle \text{ average spin along } \hat{z}
$$
\[
L(x) = \cosh x - \frac{1}{x} \quad \text{Logarithmic function}
\]

for large \(x\), \(L(x) \to 1\)

for small \(x\), \(L(x) = \frac{\cosh x}{\sinh x} - \frac{1}{x} \approx \frac{1 + \frac{x^2}{2}}{x + \frac{x^3}{6}} - \frac{1}{x} = \frac{1 + \frac{x^2}{2}}{x(1 + \frac{x^2}{6})} - \frac{1}{x}
\]

\[
= \frac{(1 + \frac{x^2}{2})(1 - \frac{x^2}{6})}{x} - \frac{1}{x} \approx \frac{1 + \frac{x^2}{2} - \frac{x^2}{6}}{x} - \frac{1}{x}
\]

\[
\approx \frac{x}{3}
\]

So, \(L(x) \approx 1 - \frac{x}{3}\)

\(x = \beta \mu h\)

\(\Rightarrow \) at small \(h\) or at large \(T\) (small \(\beta\))

\[
\langle \mu_3^2 \rangle = \frac{\mu^2 \beta h}{3} = \frac{\mu^2 h}{3 k_B T}
\]

\[
M_3^2 = \frac{N \mu^2 h}{3 k_B T}
\]

Magnetic susceptibility \(\chi = \lim_{T \to 0} \frac{\partial M_3^2}{\partial H} = \frac{N \mu^2}{3 k_B T} \propto \frac{1}{T}
\]

Curie law of paramagnetism

\(\chi \propto \frac{1}{T}\)